Facile Redistribution of Trialkyl Silanes Catalyzed by Iridium Silyl Complexes

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Supporting Information

^{1}H, $^{13}C\{^{1}H\}$, and $^{29}Si\{^{1}H\}$ NMR Spectra of Alkyl Scrambling Products From Trialkyl Silanes

(* and Ar indicate solvent and aromatic resonances, respectively.)

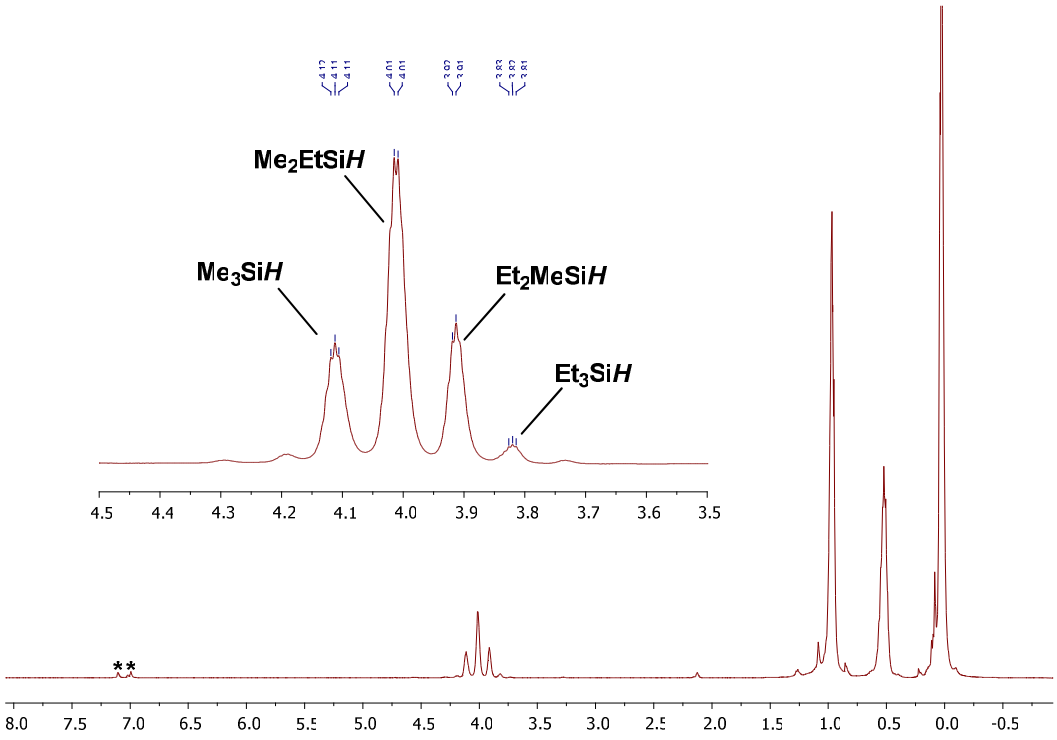


Figure S1. ^{1}H NMR (toluene-d_8) spectrum of the alkyl redistribution products obtained from Me_2EtSiH.

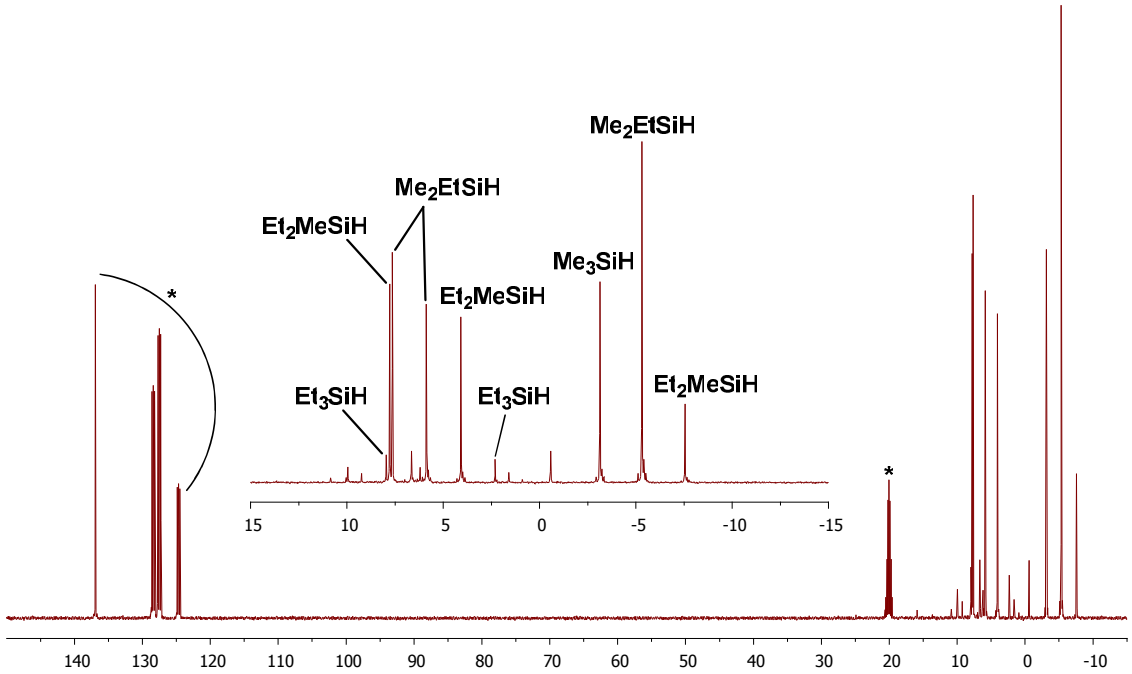


Figure S2. ^{13}C{^{1}H} NMR (toluene-d_8) spectrum of the alkyl redistribution products obtained from Me_2EtSiH.

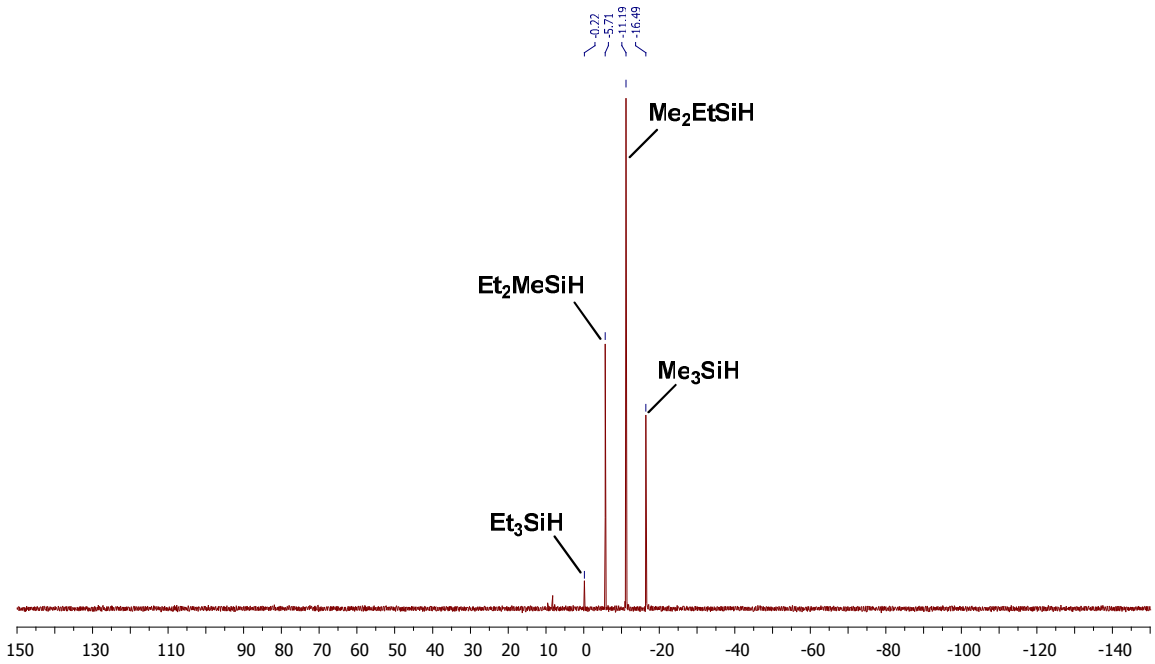


Figure S3. $^{29}Si\{^{1}H\}$ NMR (toluene-d_8) spectrum of the alkyl redistribution products obtained from Me_2EtSiH.

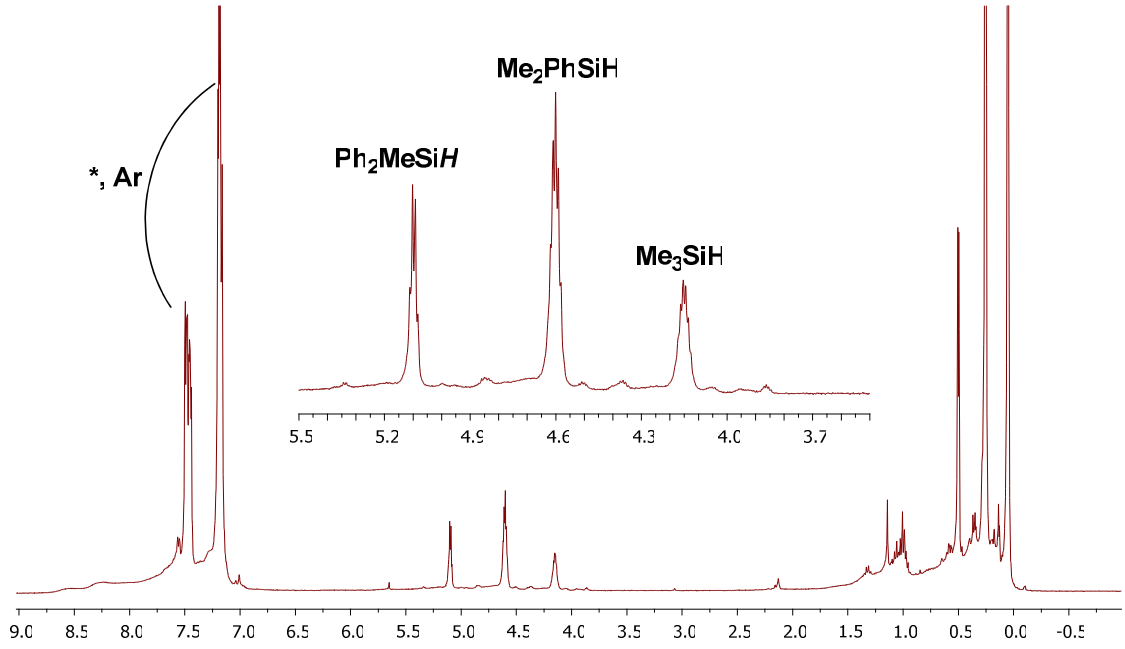


Figure S4. ^{1}H NMR (toluene-d_8) spectrum of the alkyl redistribution products obtained from Me_2PhSiH.

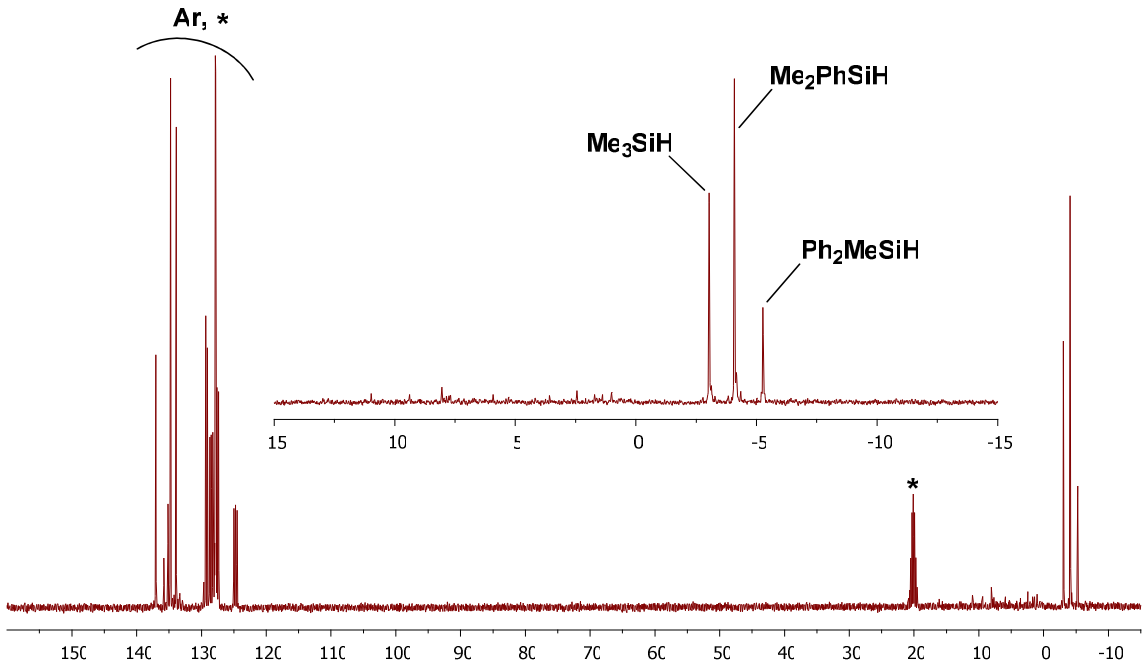


Figure S5. $^{13}C\{^{1}H\}$ NMR (toluene-d_8) spectrum of the alkyl redistribution products obtained from Me_2PhSiH.

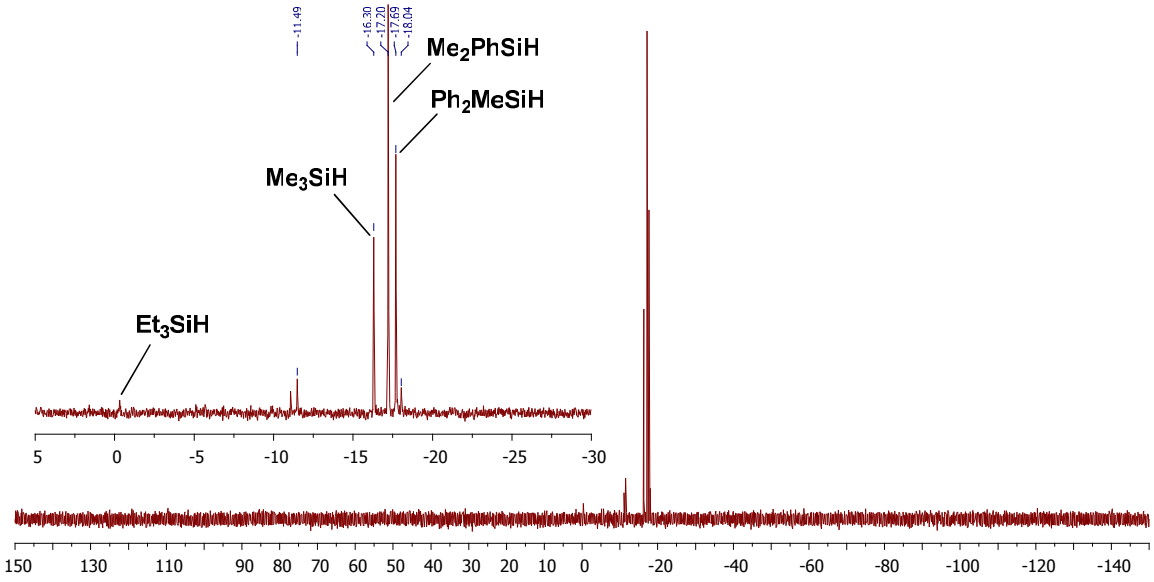


Figure S6. $^{29}Si\{^{1}H\}$ NMR (toluene-d_8) spectrum of the alkyl redistribution products obtained from Me_2PhSiH.

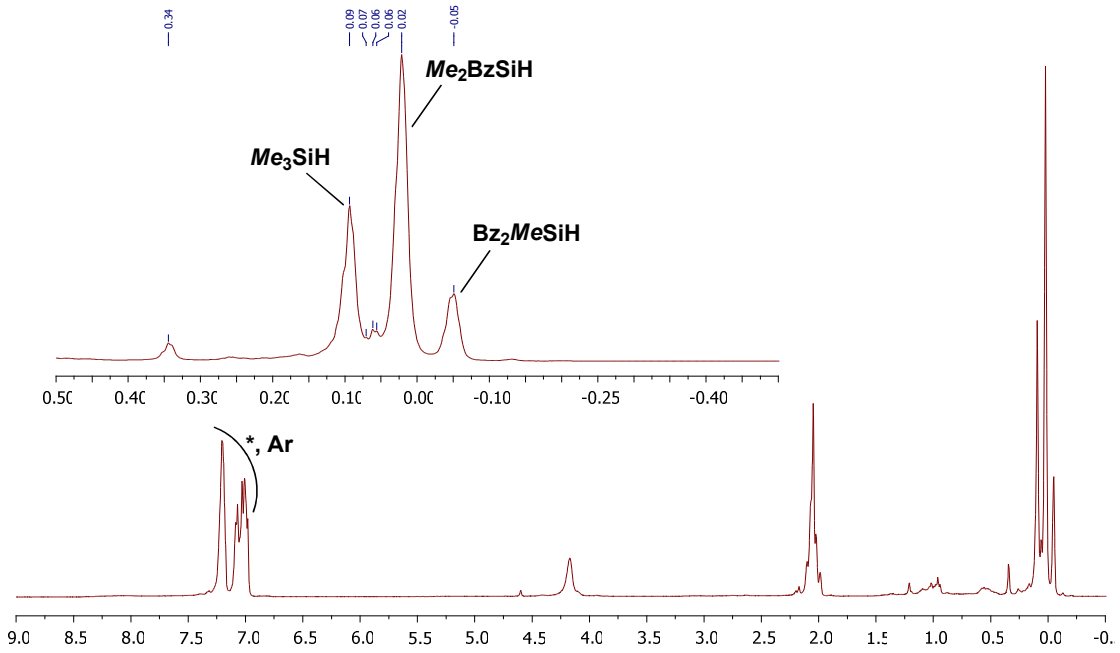


Figure S7. ^{1}H NMR (C_6D_6) spectrum of the alkyl redistribution products obtained from Me_2BzSiH.

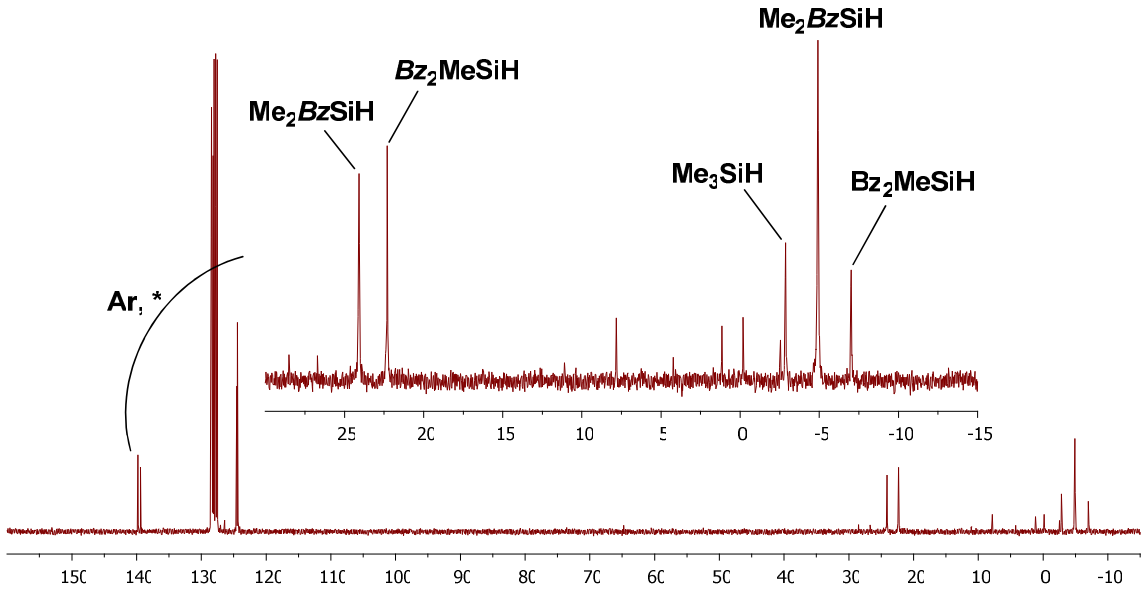


Figure S8. $^{13}C\{^{1}H\}$ NMR (C_6D_6) spectrum of the alkyl redistribution products obtained from Me_2BzSiH.

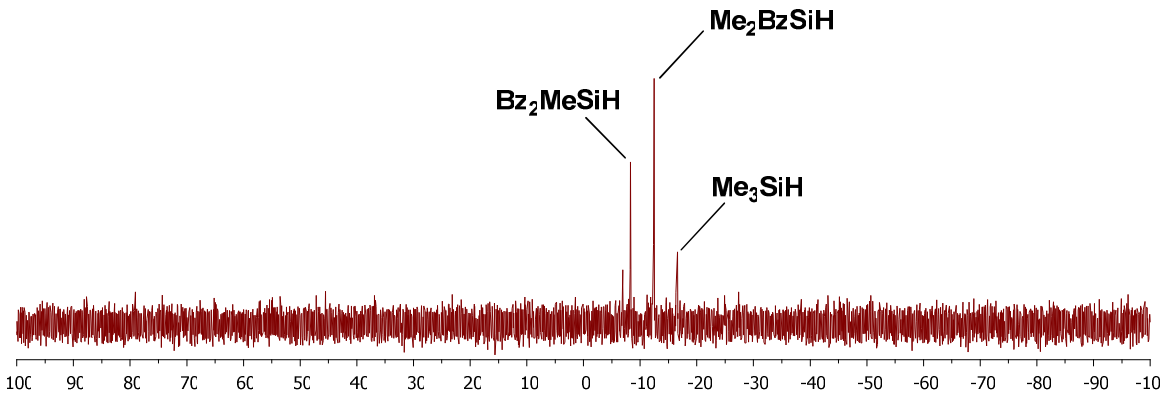


Figure S9. $^{29}Si\{^{1}H\}$ NMR (C_6D_6) spectrum of the alkyl redistribution products obtained from Me_2BzSiH.

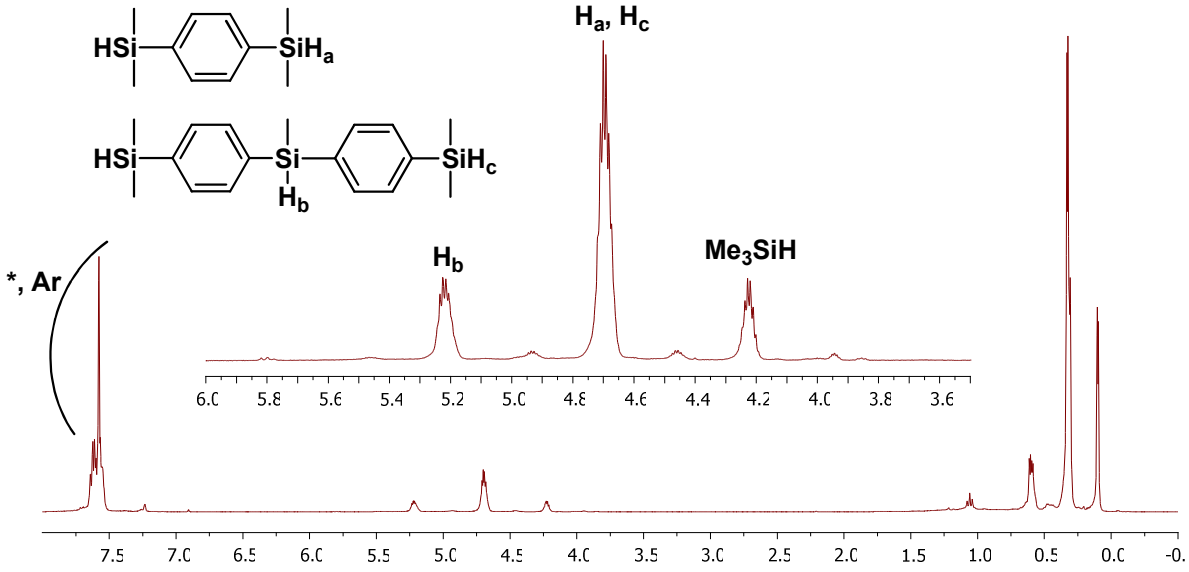


Figure S10. ^{1}H NMR (C_6D_6) spectrum of the alkyl redistribution products obtained from 1,4-bis(dimethylsilyl)benzene.

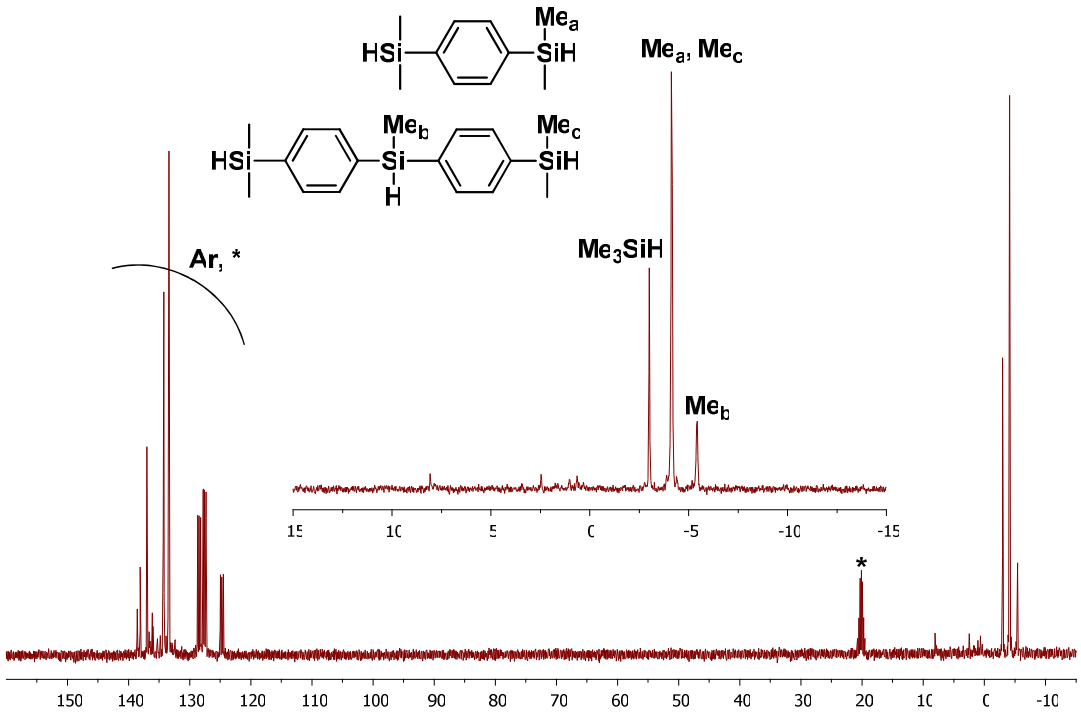


Figure S11. $^{13}C\{^{1}H\}$ NMR (C_6D_6) spectrum of the alkyl redistribution products obtained from 1,4-bis(dimethylsilyl)benzene.

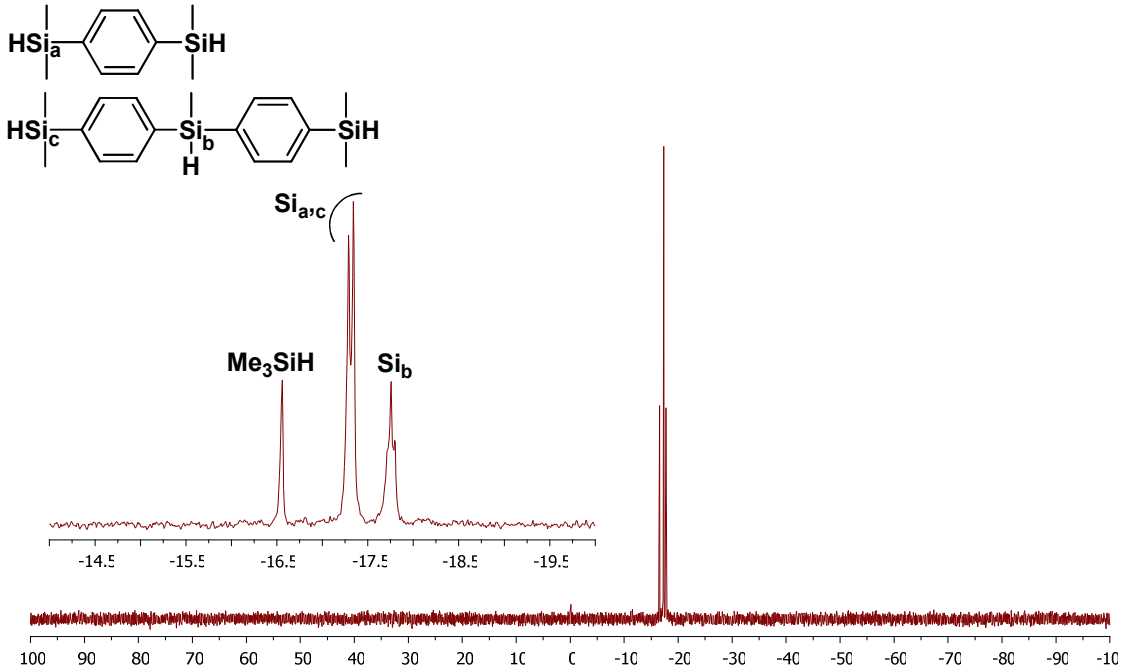


Figure S12. $^{29}Si\{^{1}H\}$ NMR (C_6D_6) spectrum of the alkyl redistribution products obtained from 1,4-bis(dimethylsilyl)benzene.

^{1}H, $^{13}C\{^{1}H\}$, and $^{29}Si\{^{1}H\}$ NMR Spectra of Complex 1 and a HSQC of Complex 2

(* indicates solvent resonance.)

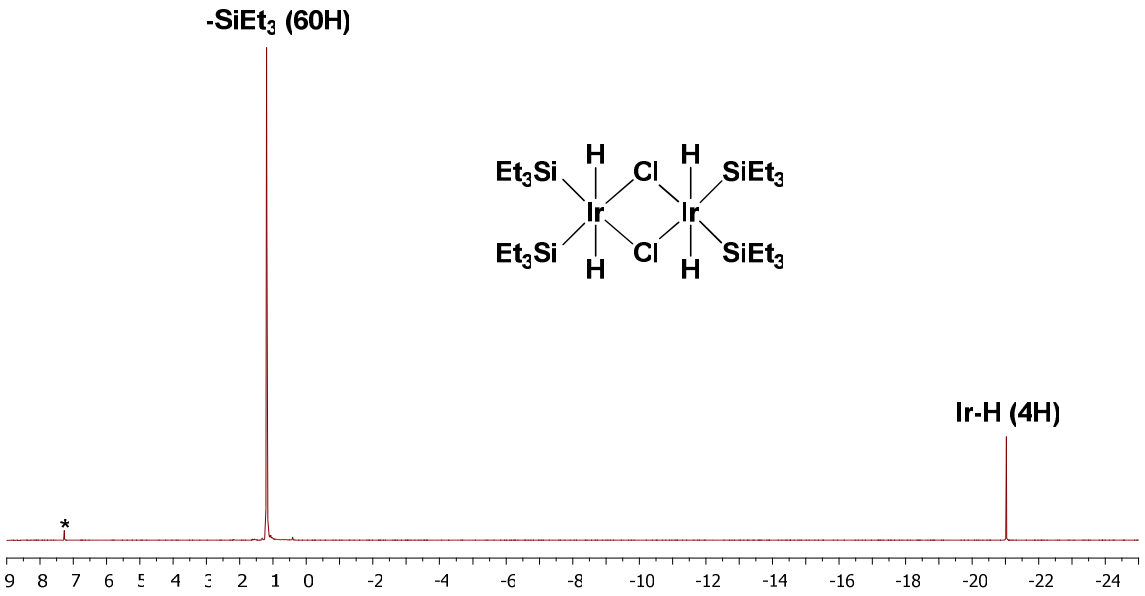


Figure S13. ^{1}H NMR (C_6D_6) spectrum of complex **1**.

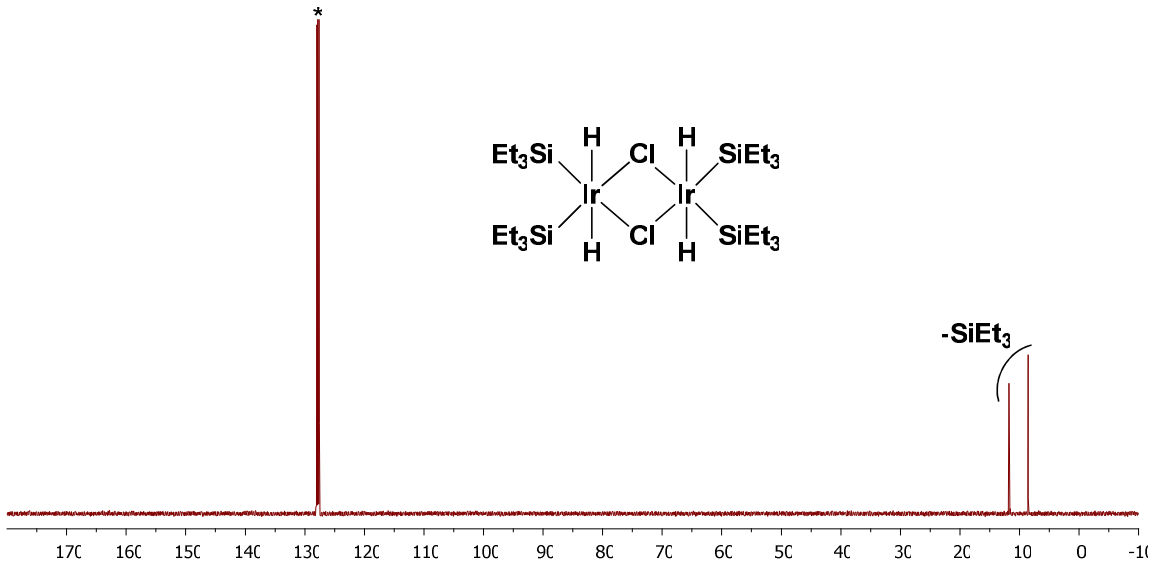


Figure S14. $^{13}C\{^{1}H\}$ NMR (C_6D_6) spectrum of complex **1**.

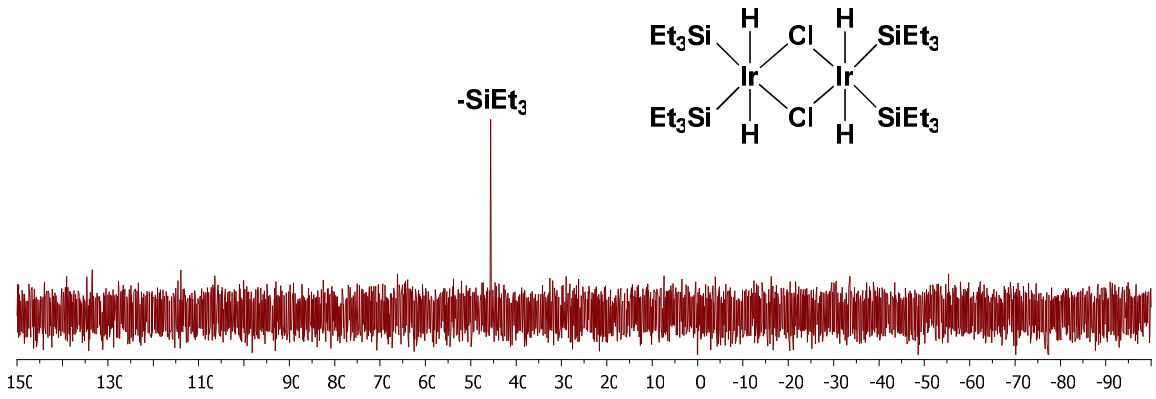


Figure S15. $^{29}Si\{^{1}H\}$ NMR (C_6D_6) spectrum of complex **1**.

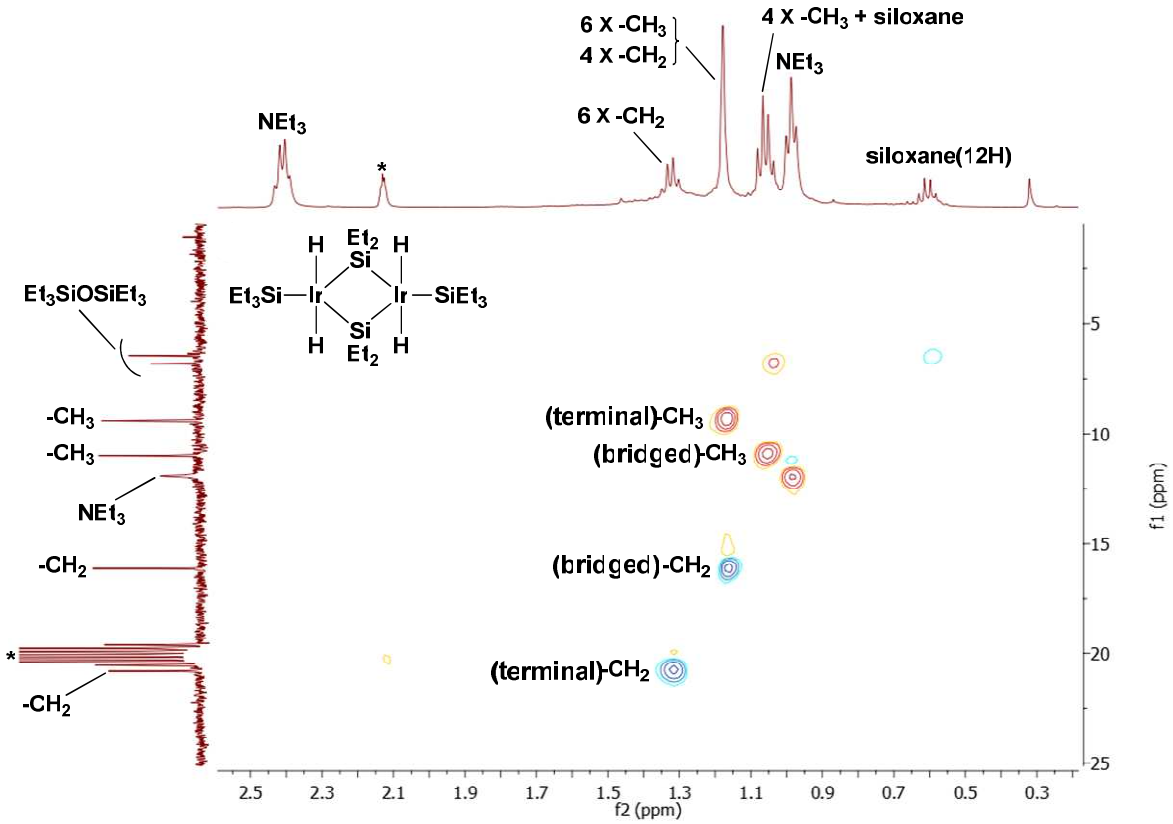


Figure S16. HSQC (toluene-d_8) spectrum of complex **2**.

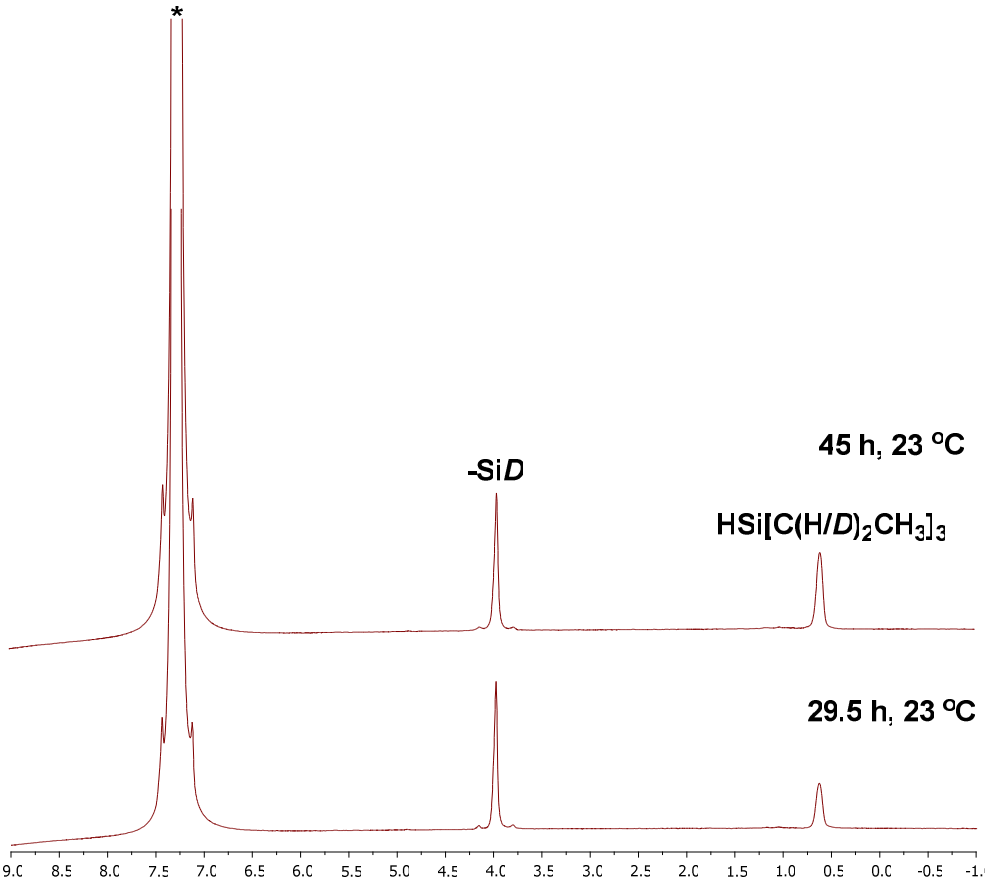
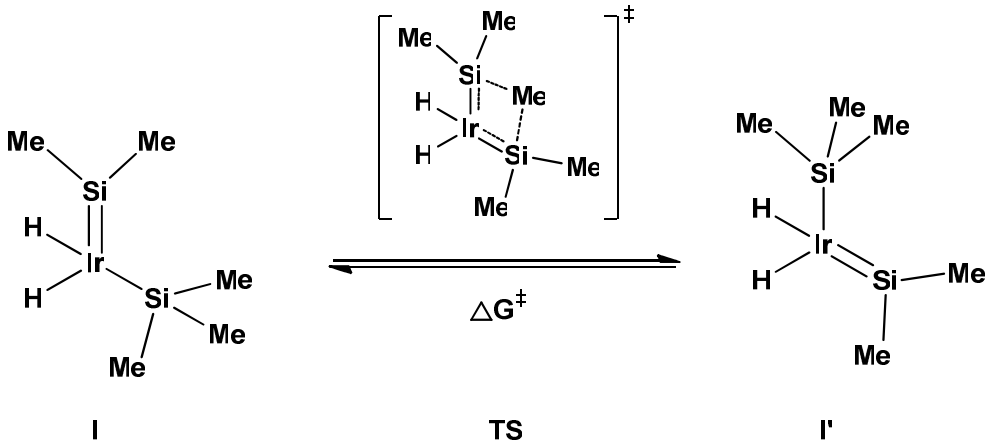


Figure S17. ^{2}H NMR (C_6H_6) spectrum of the reaction mixture (Figure 4).

Computational Details. All density functional theory (DFT) calculations have been performed with Gaussian09 suite of program[1] with a tight self-consistent field convergence threshold for both gradient and wave function convergence. The computational studies were carried out on $[Ir(H)_2(SiMe_3)(SiMe_2]$, **3**, as well as on the product after the methyl migration. For each complex, structural data are presented for two distinct minima in which the hydride is oriented cis (**I**) and trans (**II**) to the each other (Table S4~S7). Frequency calculations were carried out on all minimum structures, and the resulting frequencies all had positive values. No zero point correction was added for the energies presented in the table. All geometries were fully optimized at the DFT level, using the hybrid B3LYP exchange-correlation functional[2-6] and the newly developed m062x methods.[7] In terms of basis sets, the double-ζ quality 6-311+G* and LanL2DZ were employed for the lighter nonmetallic atoms in ligands (such as C, Si, and H atoms) and the Ir atom, respectively. A relativistic effective core potential (ECP) for Ir atom replaces the inner core electrons leaving the outer layer $[(5s^2)(5p^6)]$ electrons and the $(5d^6)$ valence electrons.[8-10] This combination of basis set is adequate to describe the ground and excited state geometries of the Ir(III) complexes, and it has been verified and discussed elsewhere. Continuum solvent model with conductor-like polarizable continuum model of electrostatics (CPCM) was used to account for solvent effects.[11]



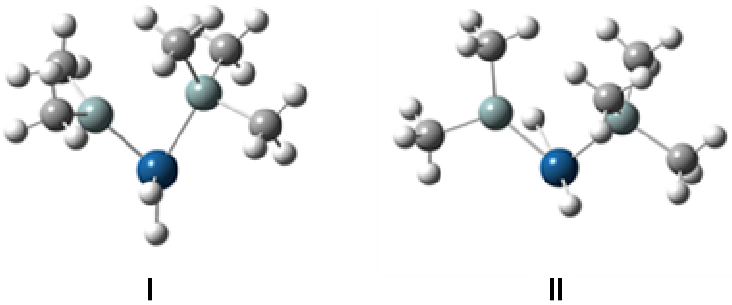


Figure S18. DFT calculation scheme of methyl migration for $Ir(SiMe_3)H_2(SiMe_2)$, *cis* (**I**) and *trans* (**II**) according to coordinated hydride.

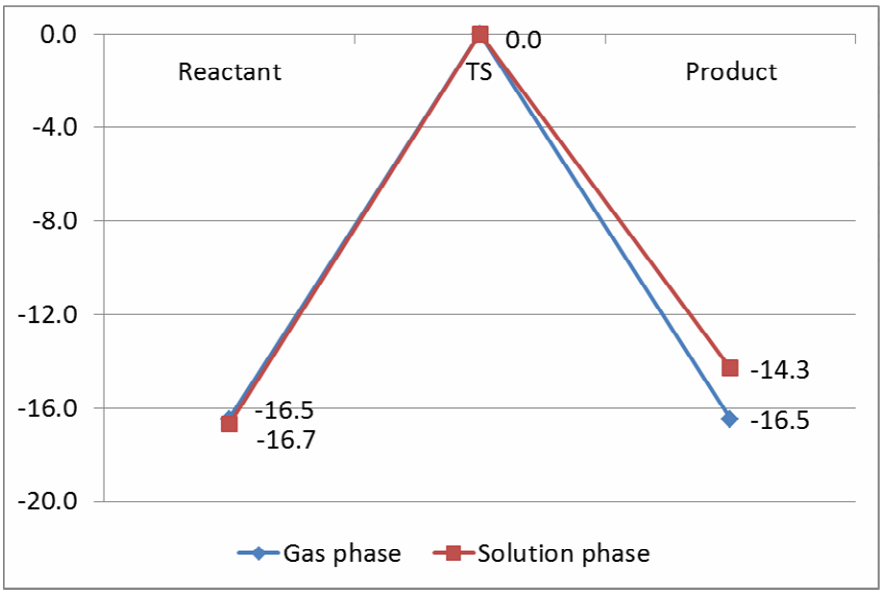


Figure S19. Diagram of relative energy of reactants, transition state and product of methyl migration for $Ir(SiMe_3)H_2(SiMe_2)$ complex in gas and solvent phase by B3LYP.

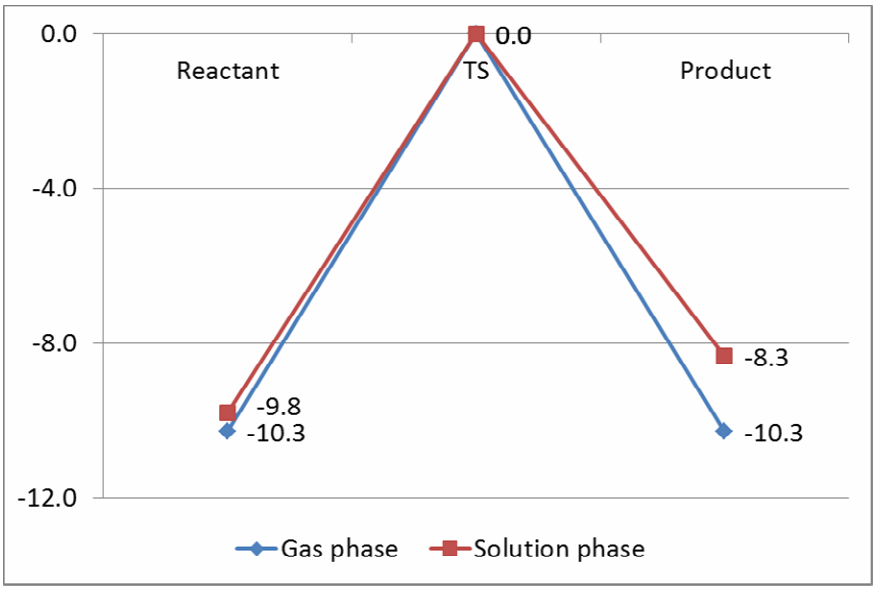


Figure S20. Diagram of relative energy of reactants, transition state and product of methyl migration for $Ir(SiMe_3)H_2(SiMe_2)$ complex in gas and solvent phase by m06-2x.

Reference

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Table S1. Selected bond lengths (Å) and angles (°) of $Ir(SiMe_3)H_2(SiMe_2)$, I from DFT studies by B3LYP[a]

	Gas phase				Solution phase(in Toluene)			
	Reactant		TS		Reactant		TS	
	Basis 1	Basis 2	Basis 1	Basis 2	Basis 1	Basis 2	Basis 1	Basis 2
Ir-$Si_1(SiMe_3)$	2.434	2.435	2.287	2.310	2.415	2.449	2.277	2.298
Ir-$Si_2(SiMe_2)$	2.187	2.187	2.287	2.310	2.168	2.179	2.297	2.323
Ir-H_1	1.551	1.551	1.554	1.553	1.555	1.554	1.557	1.556
Ir-H_2	1.667	1.667	1.698	1.684	1.692	1.679	1.718	1.702
Si_1-Ir-Si_2	83.41	83.41	64.15	63.97	82.36	83.68	64.44	64.26
H_1-Ir-H_2	84.98	84.98	86.50	85.01	87.79	86.64	87.69	86.34

[a]Basis set employed in the calculation. Basis set 1 consists of 6-311+G* on C, H atoms and 6-311++G(3df,3pd) on Si atom but Ir LanL2DZ. Basis set 2 consists of 6-311+G* on all atoms but Ir LanL2DZ.

Table S2. Selected bond lengths (Å) and angles (°) of $Ir(SiMe_3)H_2(SiMe_2)$, I from DFT studies by m06-2x[a]

	Gas phase				Solution phase(in Toluene)			
	Reactant		TS		Reactant		TS	
	Basis 1	Basis 2	Basis 1	Basis 2	Basis 1	Basis 2	Basis 1	Basis 2
Ir-$Si_1(SiMe_3)$	2.382	2.419	2.247	2.310	2.415	2.449	2.247	2.267
Ir-$Si_2(SiMe_2)$	2.138	2.149	2.247	2.310	2.168	2.179	2.247	2.267
Ir-H_1	1.536	1.535	1.537	1.553	1.555	1.554	1.537	1.537
Ir-H_2	1.669	1.653	1.707	1.684	1.692	1.679	1.707	1.690
Si_1-Ir-Si_2	74.87	74.88	64.76	63.97	82.36	83.68	64.76	64.59
H_1-Ir-H_2	87.61	85.73	88.13	85.01	87.79	86.64	88.13	85.36

[a]Basis set employed in the calculation. Basis set 1 consists of 6-311+G* on C, H atoms and 6-311++G(3df,3pd) on Si atom but Ir LanL2DZ. Basis set 2 consists of 6-311+G* on all atoms but Ir LanL2DZ.

Table S3. Total electronic energies and Gibbs free energies of calculated structures, in Hartrees[a]

		Gas phase		Solution phase(in Toluene)	
		TE	Gibbs FE	TE	Gibbs FE
B3LYP	Reactants	-884.6182	-884.4634	-884.6308	-884.4758
	TS	-884.5961	-884.4372	-884.6081	-884.4492
M06-2x	Reactants	-884.2625	-884.1042	-884.2756	-884.1164
	TS	-884.2495	-884.0878	-884.2619	-884.1008

[a]Basis set 1 consists of 6-311+G* on C, H atoms and 6-311++G(3df,3pd) on Si atom but Ir LanL2DZ.

Table S4. Cartesian coordinates (Å) for the optimized structure of $Ir(SiMe_3)H_2(SiMe_2)$, I
Gas phase Energy: -884.6077886 hartrees(by B3LYP), -884.2625448 hartrees(by M06-2x)
Solution phase Energy: -884.6308204 hartrees(by B3LYP), -884.2704095 hartrees(by M06-2x)
Zero Point Energy: 128.2856 kcal/mol(Gas,M06-2x), 125.4832 kcal/mol(Solution, M06-2x)
Coordinate:

	x	y	z
Ir 1	0.166132	-1.035808	0.025992
Si 2	-1.364842	0.78954	-0.00621
Si 3	1.388908	0.71764	-0.0116
C 4	-1.944038	1.145357	1.755891
H 5	-1.180116	1.677419	2.331163
H 6	-2.842845	1.770981	1.746241
H 7	-2.189323	0.230912	2.303529
C 8	-1.086688	2.494957	-0.79308
H 9	-0.733845	2.417711	-1.82606
H 10	-2.028868	3.052976	-0.81185
H 11	-0.36722	3.114719	-0.24457
C 12	-2.802934	0.033673	-0.962
H 13	-3.684671	0.680573	-0.89875
H 14	-2.554077	-0.093741	-2.01842
H 15	-3.082044	-0.948664	-0.57031
C 16	2.174232	1.486613	-1.51623
H 17	2.098895	2.577144	-1.4672
H 18	3.24	1.239416	-1.54892
H 19	1.714654	1.143065	-2.44278
C 20	2.129359	1.548598	1.491375
H 21	3.222371	1.519284	1.456231
H 22	1.839628	2.605243	1.502989
H 23	1.798107	1.095527	2.426266

H 24	0.281764	-1.014492	-1.50545
H 25	0.51896	-2.666538	-0.03998

Table S5. Cartesian coordinates (Å) for the optimized structure in the transition state in methyl migration, I

	x	y	z
Ir 1	0.100636	-0.914643	-0.22213
Si 2	0.018019	-1.141686	2.011343
Si 3	-0.00926	-3.031695	0.522357
C 4	-1.574579	-0.66435	2.879713
H 5	-2.415136	-1.276359	2.542511
H 6	-1.499595	-0.755291	3.967146
H 7	-1.819225	0.376091	2.647979
C 8	0.174761	-3.211047	2.690878
H 9	1.226113	-3.40001	2.911438
H 10	-0.297468	-2.836915	3.604662
H 11	-0.317016	-4.178408	2.548277
C 12	1.488262	-0.575323	3.013079
H 13	1.387631	-0.819595	4.073927
H 14	2.415716	-1.012876	2.638006
H 15	1.581939	0.51071	2.921482
C 16	1.436796	-4.163773	0.185829
H 17	2.37687	-3.712763	0.510156
H 18	1.326095	-5.135966	0.673429
H 19	1.512423	-4.330719	-0.89261
C 20	-1.621961	-3.959372	0.283524
H 21	-1.56061	-4.996576	0.625372
H 22	-2.447167	-3.473671	0.810693
H 23	-1.881147	-3.973172	-0.7789
H 24	1.630332	-1.022976	-0.11265
H 25	0.325847	0.132323	-1.5515

Table S6. Cartesian coordinates (Å) for the optimized structure of $Ir(SiMe_3)H_2(SiMe_2)$, II

Gas phase Energy: -884.6347474 hartrees(by B3LYP), -884.2898792hartrees(by M06-2x)
Solution phase Energy: -884.6441802 hartrees(by B3LYP), -884.3050185 hartrees(by M06-2x)
Zero Point Energy: 128.2825 kcal/mol(Gas,M06-2x), 127.9361kcal/mol(Solution, M06-2x)

	x	y	z
Ir 1	-0.171112	-0.854599	-0.03027
Si 2	1.668354	0.542954	0.041879
Si 3	-1.740903	0.667608	-0.05319
C 4	1.805848	1.628947	1.585618
H 5	1.793523	1.024938	2.49766
H 6	2.746942	2.192333	1.572923
H 7	0.991651	2.355406	1.664401
C 8	3.200768	-0.58031	0.011545
H 9	3.187689	-1.278972	-0.83148
H 10	4.110307	0.025812	-0.08481
H 11	3.288907	-1.170488	0.92796
C 12	1.838235	1.667596	-1.47854
H 13	2.771045	2.242265	-1.41855
H 14	1.877233	1.078398	-2.40029
H 15	1.020987	2.385353	-1.58862
C 16	-1.672117	2.536501	-0.05441
H 17	-2.357035	2.930702	-0.8134
H 18	-2.016361	2.915351	0.913938
H 19	-0.679825	2.943055	-0.24379
C 20	-3.531562	0.163495	0.20929
H 21	-3.885292	0.506525	1.187237
H 22	-4.176461	0.623722	-0.54789
H 23	-3.669412	-0.918747	0.162471
H 24	0.50875	-1.469707	1.300568
H 25	-1.168357	-0.027086	-1.45068

Table S7. Cartesian coordinates (Å) for the optimized structure in the transition state in methyl migration, II in the gas phase

	x	y	z
Ir 1	0.399722	-0.646402	-1.50208
Si 2	-1.28347	0.359611	-0.45796
Si 3	1.233438	0.783576	-0.01937
C 4	-2.181991	1.786709	-1.29387
H 5	-2.704813	1.403733	-2.17686
H 6	-2.928851	2.254306	-0.64313
H 7	-1.492689	2.558526	-1.64412
C 8	-2.542231	-0.641505	0.514598
H 9	-2.063125	-1.348106	1.194627
H 10	-3.229862	-0.008792	1.084956
H 11	-3.141706	-1.226395	-0.19226
C 12	-0.417218	1.361727	1.260696
H 13	-1.369752	1.902676	1.23969
H 14	-0.447741	0.653245	2.088574
H 15	0.269198	2.171465	1.531707
C 16	1.852607	2.468016	-0.58638
H 17	2.15638	3.108291	0.248951
H 18	2.727339	2.324122	-1.22953
H 19	1.106921	3.001375	-1.1805
C 20	2.353451	0.177192	1.363191
H 21	2.574292	0.960535	2.095441
H 22	1.930481	-0.684608	1.882542
H 23	3.305818	-0.142319	0.925067
H 24	0.49147	0.359609	-2.87498
H 25	0.358867	-1.784723	-0.25757